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Phase Behavior and Substitution Limit of Mixed Cesium-Formamidinium Lead Tri-Iodide Perovskites.

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ABSTRACT: The mixed cation lead iodide perovskite photovoltaics show improved stability following site substitution of cesium ions (Cs⁺) onto the formamidinium cation sites (FA⁺) of (CH(NH₂)₂PbI₃ (FAPbI₃), and increased resistance to formation of the undesirable δ -phase. The structural phase behavior of Cs_{0.1}FA_{0.9}PbI₃ has been investigated by neutron powder diffraction (NPD), complemented by single crystal and power X-ray diffraction, and photoluminescence spectroscopy. The Cs substitution limit has been determined to be less than 15% and the cubic α -phase Cs_{0.1}FA_{0.9}PbI₃ is shown to be synthesizable in bulk and stable at 300 K. On cooling cubic Cs_{0.1}FA_{0.9}PbI₃ a slow, second order cubic to tetragonal transition is observed close to 290 K, with variable temperature NPD indicating the presence of the tetragonal β -phase, adopting the space group $P4/mbm$, between 290 K and 180 K. An orthorhombic phase or twinned tetragonal phase is formed below 180 K and the temperature for the further transition to a disordered state is lowered to 125 K compared to that seen in phase pure α -FAPbI₃ (140 K). These results demonstrate the importance of understanding the effect of cation site substitution on structure-property relationships in perovskite materials.

1. INTRODUCTION:

The popularity of hybrid halide perovskites has skyrocketed over recent years due to significant improvements to already impressive photovoltaic (PV) device efficiencies¹. A vast array of perovskite compositions have been explored, the most effective taking on an ABX₃ structure where the A, B and X-sites are occupied with an organic cation, lead and a halide anion respectively². However, perovskite devices have been plagued with stability problems³. One of the archetypical PV perovskites, formamidinium lead iodide (CH(NH₂)₂PbI₃, FAPbI₃), has been found to be too unstable for use in commercial devices, forming a PV-inactive yellow hexagonal δ -phase at room temperature and only stabilizing as the black cubic α -phase above 60 °C⁴⁻⁷. In recent years cesium lead iodide (CsPbI₃) has also been investigated, although in a similar fashion to FAPbI₃, CsPbI₃ transitions from the desirable α -perovskite phase to a yellow PV-inactive, non-perovskite δ -phase under ambient conditions⁸⁻¹⁰.

In the drive to improve PV device efficiencies and lifetimes, numerous studies have demonstrated that chemical site substitution at one or more of the perovskites' A, B or X sites can improve the material's stability and PV performance¹¹⁻¹⁴. Incorporating small amounts of Cs at the FA site

of the FAPbI₃ structure can significantly improve device lifetimes, enhancing the thermal and moisture stability of thin films when compared to pure FAPbI₃¹⁵. Yi *et al.* attributed the enhanced stability provided by the Cs cation to the improved crystallization of the α -phases, as cation mixing in the α -phase is more energetically favorable than that in the δ -phase for the CsPbI₃ and FAPbI₃ structure types¹⁶. However, there is confusion concerning the structures of the mixed Cs-FA lead iodide perovskites, with contradictory information on whether the composition Cs_{0.1}FA_{0.9}PbI₃ adopts a tetragonal or cubic structure at room temperature¹⁷⁻²⁰, and the phase behavior of the mixed Cs-FA cation perovskite remains poorly understood. It is crucial that the fundamental structural properties of these mixed Cs-FA cation materials are fully understood in order to appreciate PV device operation across different environments.

The phase behavior as a function of temperature of the parent material formamidinium lead iodide (FAPbI₃) has been described in previous work³². Results from neutron powder diffraction and synchrotron X-ray diffraction experiments are consistent with the formation of two low temperature phases related to the room temperature cubic phase of α -FAPbI₃. The first transition to a primitive tetragonal cell (β -FAPbI₃) occurs just below room temperature at

~285 K and is associated with restricted motion of the FA⁺ cations. On cooling below 140 K, a further phase transition occurs to Y-FAPbI₃ in which the FA⁺ cation positions demonstrate a high level of disorder in a glassy state - though some elements of long-range ordering of the cations or tilting of the PbI₆ octahedra persists.

In this paper we present a detailed overview of the phase behavior of mixed Cs-FA lead iodide perovskites between 300 and 100 K using neutron powder diffraction, complemented with X-ray diffraction (single crystal and powder) and variable temperature photoluminescence. Significant quantities of mixed cation perovskite powders were synthesized based on the method of Poglitsch and Weber²² and single crystals of the same compositions were grown according to the method of Saidaminov *et al.*^{23,24}. It was found that no more 15% Cs could be incorporated into the FAPbI₃ structure through the synthetic methods used, therefore a single phase of the composition Cs_{0.1}FA_{0.9}PbI₃ was investigated in this work in detail. Inclusion of 10% Cs into methylammonium and formamidinium perovskites for use in PV devices is frequently reported in the literature due to the significantly improved PV performance; this serves as an additional incentive to focus on the Cs_{0.1}FA_{0.9}PbI₃ composition^{15,16,25}. The quality and composition of the synthesized samples were checked through powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Differential scanning calorimetry (DSC) was initially used to check for potential phase transition temperatures.

2. MATERIALS AND METHODS:

2.1 Materials Synthesis: Hydrogenous formamidinium iodide (FAI-H) was purchased from GreatCell Solar, all other reagents were purchased from Merck and solvents were purchased from Alfa Aesar (unless specified otherwise), with purities >99%.

Cs_{0.1}FA_{0.9}PbI₃-H powder. Precipitation of the mixed cation perovskite Cs_{0.1}FA_{0.9}PbI₃ was based on the method by Poglitsch and Weber²². 0.0810 g (3.12×10⁻⁴ moles) of cesium iodide (CsI), 0.4823 g (2.82×10⁻³ moles) of formamidinium iodide (FAI-H) and 1.4367 g (3.12×10⁻³ moles) of lead iodide (PbI₂) were added to 3.12 ml of HI (+1.5 wt% H₃PO₄) in a three necked flask fitted with a condenser and nitrogen gas inlet, thereby forming a reaction mixture with the molar ratios Cs:FA:Pb of 0.1:0.9: 1.0. The solution was heated to 100 °C under nitrogen and stirring, the stirring was then stopped, and the solution kept at 100 °C for 45 minutes before being cooled to 45 °C over 1 hour. The resulting powder was filtered, and oven dried at 100 °C overnight. See supplementary information S1 for details of reactant quantities used in the synthesis of Cs_xFA_{1-x}PbI₃ (x = 0.15, 0.2).

Cs_{0.1}FA_{0.9}PbI₃-H crystals. Crystal growth by inverse solubility of the mixed cation perovskite Cs_{0.1}FA_{0.9}PbI₃ was prepared based on the method by Saidaminov *et al.*^{23,24}. 0.0810 g (3.12×10⁻⁴ moles) of CsI, 0.4823 g (2.82×10⁻³ moles) of FAI and 1.4367 g (3.12×10⁻³ moles) of PbI₂ were dissolved at 80

°C in 3.46 ml of γ-butyrolactone (GBL). The solvent GBL had first been dried over calcium chloride (CaCl₂). The solutions were heated to 110 °C at a rate of 10 °C/hour, the growth of larger crystals could be achieved by decreasing the ramp rate. The temperature was increased to 120 °C for a further hour before the resulting crystals were filtered from the remaining solution and oven dried at 100 °C overnight. The method was repeated to achieve the desired quantity of perovskite crystals. See supplementary information S1 for details of reactant quantities used in the synthesis of Cs_xFA_{1-x}PbI₃ (x = 0.15, 0.2).

FAI-D powder. Partial deuteration of the phases of interest was attempted with the aim of reducing the level of incoherent scattering, thereby increasing data quality through a higher signal-to-noise ratio in the neutron powder diffraction study. Part-deuterated FAI was obtained by dissolving hydrogenous FAI in a large excess of D₂O under an argon atmosphere and stirring for 60 minutes, the D₂O was then evaporated and the sample dried under vacuum. The extent of deuteration was determined by the disappearance of the NH resonance in ¹H NMR spectrum. Only partial deuteration of the cation could be achieved resulting in the composition CH(ND₂)₂I.

Cs_{0.1}FA_{0.9}PbI₃-D powder. With the aim of producing a multi-gram sample of part-deuterated Cs_{0.1}FA_{0.9}PbI₃, 0.405 g (1.559×10⁻³ moles) of dried CsI, 2.412 g ((1.378×10⁻² moles)) of FAI-D and 7.184 g (1.55×10⁻² moles) of dried PbI₂ were dissolved in 25.97 ml of dimethyl sulfoxide (DMSO-d₆, from Merck 99.9% atom % D. The solution was drop cast onto preheated glass dishes at 150 °C on a hot plate in a dry box. As the solvent evaporated a black solid formed which was subsequently dried on the hotplate for a further 120 minutes. The sample was sealed under nitrogen and stored below 5 °C to reduce H-D exchange.

2.2 Characterization:

Powder X-ray diffraction (PXRD) data were collected on a Bruker Advance D8 diffractometer (Bragg-Brentano geometry) and a STOE STADI P (Debye-Scherrer geometry) using CuKα radiation (λ = 1.54060 Å). Indexing and peak fitting were carried out in GSAS-II²⁶ on Cs_{0.1}FA_{0.9}PbI₃ samples synthesized via inverse solubility (subsequently ground using a pestle and mortar) and the precipitation method.

Single crystal X-ray diffraction (SXRD) data were collected on a RIGAKU SuperNova dual tube Eos S2 CCD diffractometer using Mo (λ = 0.7107 Å) radiation. Suitable single crystals of Cs_{0.1}FA_{0.9}PbI₃ synthesized via inverse solubility were selected and measured at 300 K using an exposure of 10 s/frame, the sample was then cooled and measured at 175 K, 150 K and 120 K using an increased exposure of 20 s/frame. The structure was solved using the programs Olex2²⁷, ShelXL²⁸ and PLATON²⁹.

Neutron powder diffraction (NPD) was carried out on the POLARIS³⁰ instrument at the ISIS Neutron and Muon Source, Rutherford Appleton Laboratories. Approximately 6 g of Cs_{0.1}FA_{0.9}PbI₃-D was loaded into a 5 mm vanadium

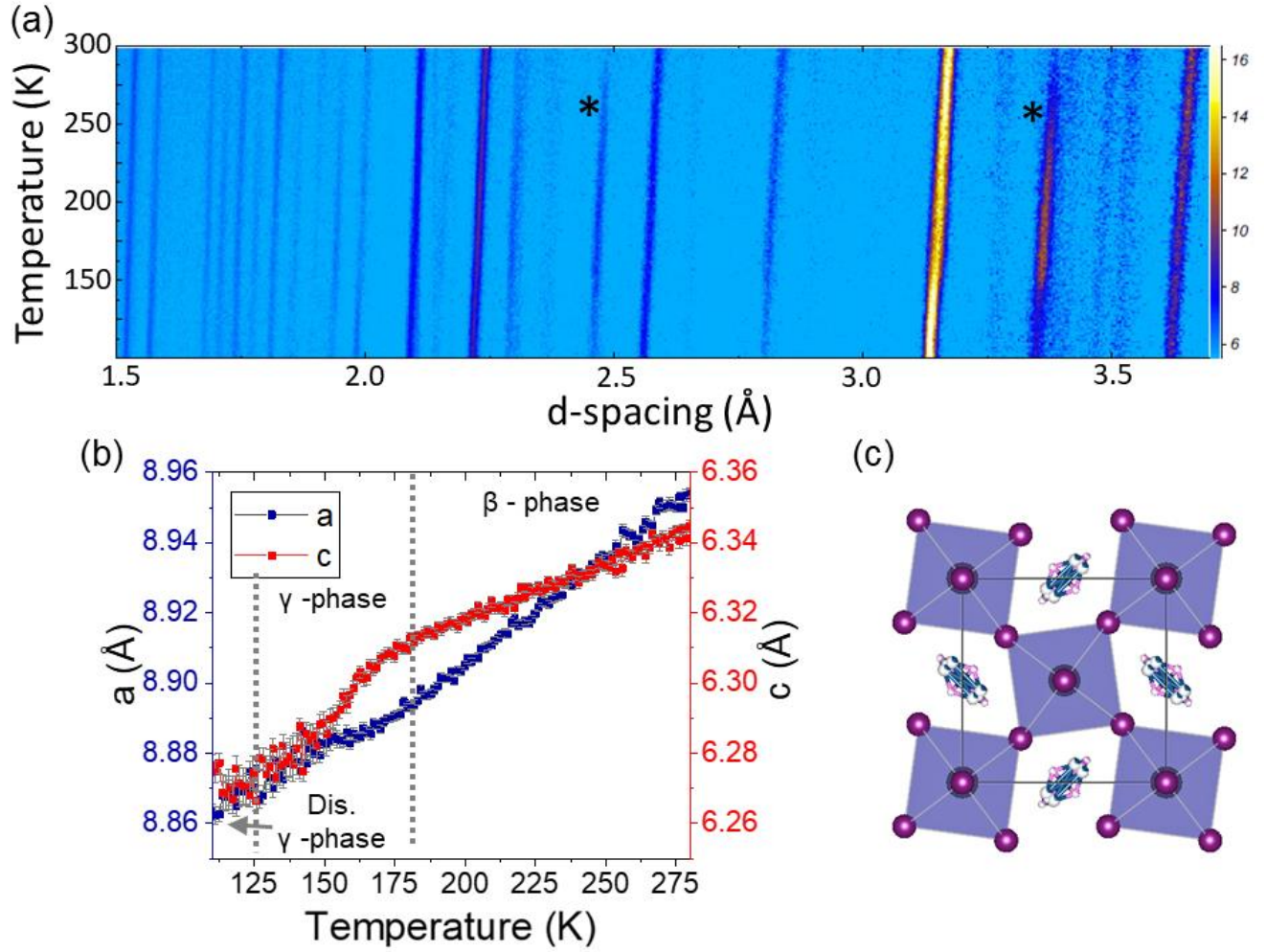


Figure 1. (a) Contour plot of neutron powder diffractograms on a $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ -D sample stacked by temperature recorded on POLARIS at ISIS neutron and muon source: * indicates prominent emergent peaks. (b) Sequential refinement of pseudo-tetragonal cell from 280 K to 110 K with transition temperatures marked by dashed grey lines. (c) Tetragonal model of the β -phase used in the sequential refinement. The model failed to fit data above 280 K coinciding with the gradual second order transition to the α -phase.

sample can under argon and sealed using an indium O-ring. The sample was cooled to 100 K in the instrument cryofurnace and data were collected over 2 hours. The sample was subsequently heated at 1 K/min to 175 K, where a second 2-hour collection was recorded, before being cooled to 110 K at 1 K/min. Variable temperature diffraction data were recorded with an exposure time of 5 mins at a ramp rate of 0.2 K/min. A final 2-hour collection was measured at 300 K.

Energy-dispersive X-ray (EDX) spectroscopy was carried out using a Jeol JSM-6480LV SEM equipped with an Oxford INCA X-Act SDD X-ray detector using an accelerating voltage of 20 kV. The programs INCA and AZtec from Oxford Instruments were used to analyze chemical composition.

Differential Scanning Calorimetry (DSC) measurements were carried out on $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ samples grown via inverse solubility and precipitation using a TA Instruments DSC Q20. Samples were cycled between 225 K and 420 K at a rate of 2 K/min.

Steady state and transient photoluminescence (PL) measurements were conducted using an in-house time-correlated single photon counter (TCSPC) set up. A single crystal

$\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ sample grown via inverse solubility was mounted onto a silica substrate using the polymer ZEONEX. The substrate was fixed in the CryoVac cryostat using Apezon grease and the cryostat pressure reduced to 10^{-6} mbar using a TurboDrag pump. An NKT Photonics, SuperK Extreme, EXR-20 white light laser (WLL) together with a SuperK Select acousto-optic tunable filter (AOTF) were used to provide and tune the excitation signal and an Olympus SLCPLFL 40x/0.55 long distance objective and CCD were used to collect the PL signal. Additional long pass, short pass and dichroic filters were used to block any remaining laser light, ensuring only the PL signal was recorded. The detector was calibrated using a xenon lamp.

3. RESULTS:

3.1 Cs Substitution Limit into FAPbI_3 under these synthesis conditions. Samples of nominal compositions $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ ($0 < x \leq 0.2$, $x = 0, 0.05, 0.10, 0.15$ and 0.20) were synthesized as single crystals through the inverse solubility method and as powder through the precipitation technique²²⁻²⁴. Samples of compositions up to $x = 0.1$, $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$, could be successfully synthesized as single-phase black powder and single crystals.

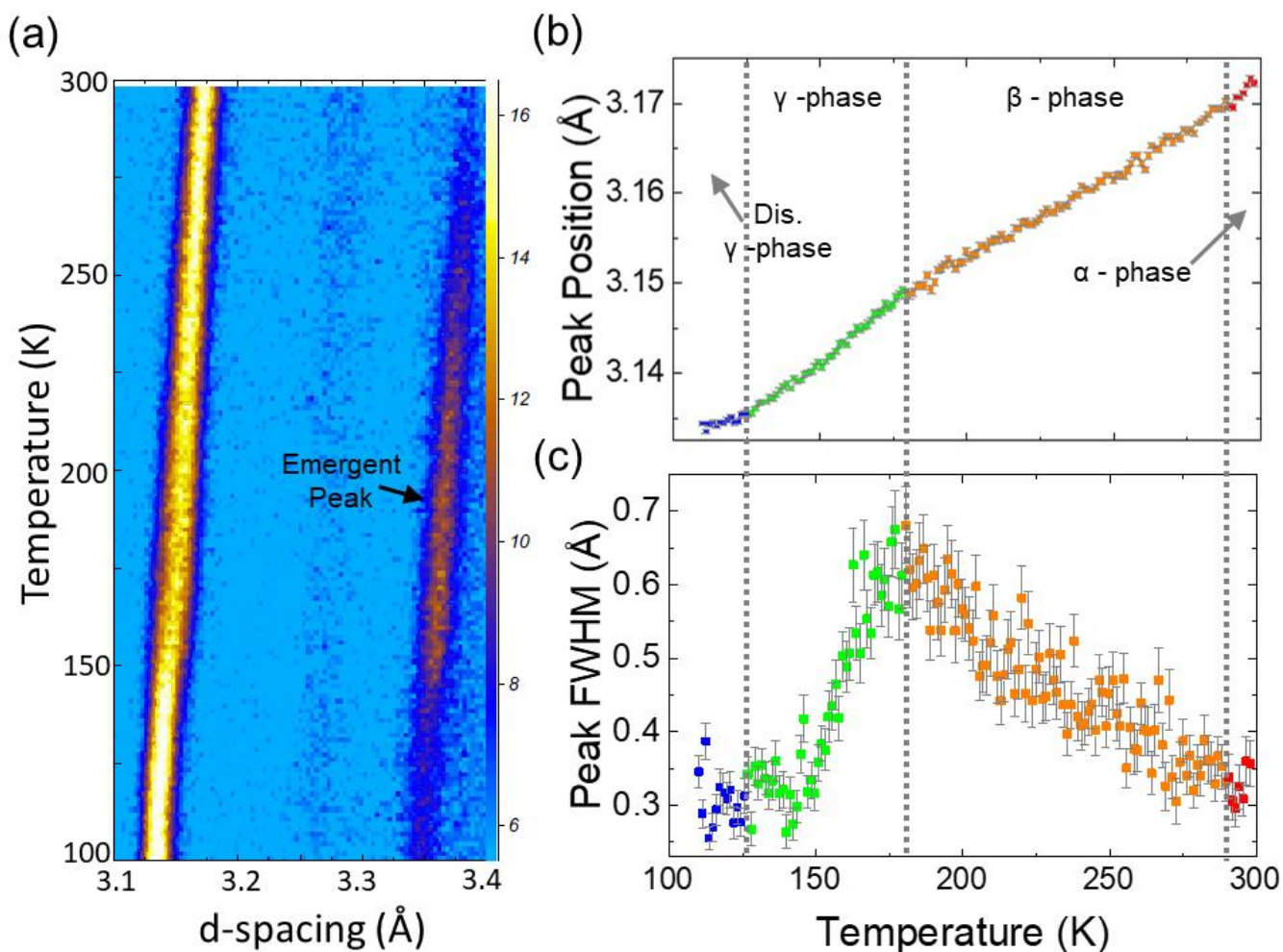


Figure 2. (a) Contour plot of neutron powder diffractograms on a $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ -D sample stacked by temperature recorded on POLARIS at ISIS neutron and muon source in the range of 3.1 - 3.4 Å. (b) Resulting peak position of the sequential peak fit on the dominant peak centered at 3.15 Å. (c) FWHM as a function of temperature of the dominant peak. (a) and (c) are divided into the cubic (red), tetragonal (orange), orthorhombic (green) and low temperature (blue) phases.

PXRD was subsequently used to support Cs incorporation into the material, which was shown by a contraction of the unit cell to 6.346 Å compared with 6.362 Å measured for pure cubic FAPbI_3 ⁷ (See supplementary information S2, S3 and S4 for PXRD, SEM, EDX Cs-maps and optical images).

$\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_3$ samples grown via the inverse solubility method in this work showed some additional peaks in PXRD data attributed to very small amounts of δ - FAPbI_3 (see supplementary information for PXRD measurements). PXRD showed $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ samples grown by inverse solubility were phase pure, whereas very small quantities (< 2%) of impurities were observed in the nominal $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ powder samples synthesized through precipitation; these could be attributed to small amounts of both δ - CsPbI_3 and δ - FAPbI_3 possibly formed post-phase formation as shown in the supplementary information Figure S3). However, single crystal and powder samples synthesized with nominal compositions $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ with $x \geq 0.15$ showed increasingly significant phase separation into black and yellow components, identified through PXRD as the α and δ -phases (Figure S2 in the supplementary information). Attempted SEM analysis of single crystals of the nominal composition

$\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_3$ showed significant levels of δ -phase needles on their surface, rendering accurate EDX compositional measurements highly unreliable. The δ -phases identified in the PXRD measurements could be indexed to both the hexagonal δ - FAPbI_3 and small quantities of the orthorhombic δ - CsPbI_3 , agreeing with previous observations³¹.

Any analysis of the product compositions using PXRD and EDX should take due account of the limitations of these methods in determining accurate and precise compositions. PXRD compositional analysis of heavy element containing phases is likely to have errors of at least 2-3% and EDX measurements will have, at least, similar or larger error margins and be highly surface sensitive. Our results demonstrate a substitution limit of less than 15% Cs, but probably above 10%, into the FAPbI_3 structure when synthesized through the inverse solubility method (see supplementary information for details regarding EDX measurements on these samples). Analysis of the single crystals using EDX suggested a preferred level of Cs inclusion near $x = 0.12 \pm 0.02$, i.e. $\text{Cs}_{0.12}\text{FA}_{0.88}\text{PbI}_3$. As the determined substitution limit was similar for both powder and crystal samples synthesized independently by the precipitation and inverse solubility methods respectively, the composition with x

slightly below the limit, i.e. $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$, was chosen for further investigation using NPD, SXRD and PL.

A limit of $x < 0.15$ for $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ is similar to that found in thin films of $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$ where MA is the cation methylammonium (CH_3NH_3^+)³² frequently employed in photovoltaic perovskites. Using solid state NMR, Kubicki *et al.* determined a 15% limit of Cs incorporation into FAPbI_3 powder, observing the appearance of additional δ - CsPbI_3 peaks for $x \geq 0.2$ ³¹. On the other hand, Prasanna *et al.* reported 25% incorporation of Cs into thin films¹⁹. It is probable that 12% Cs is the thermodynamically preferred level of incorporation for mixed Cs-FA lead iodide perovskites grown via the inverse solubility method; this limit is likely to derive from the observation that crystallization is highly dependent on the ability to form a supersaturated solution before 110 °C, the temperature at which FAPbI_3 crystallizes^{23,24}.

3.2 Variable Temperature NPD and DSC: The phase behavior of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ -D was tracked using variable temperature NPD on the POLARIS instrument at ISIS neutron and muon source. A sample of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ -D was cooled to 100 K and subsequently heated in situ at a rate of 0.2 K/min with data collected continuously and binned into 1 K ranges between 100 K and 300 K. Data from the 90° bank were used due to the range in d -spacing, resolution and count-rate matching the requirements of the experiment. Patterns with d -spacing ranging between 1.5 Å – 3.69 Å are displayed as stacked plots in Figure 1a.

A continuous shift in peak positions can be seen in Figure 1a, representing decreasing unit cell volume with decreasing temperature. Figure 1a also shows the emergence of additional peaks between 290 K and 180 K indicating decreasing symmetry from 298K. The additional peaks represent the emergence of the tetragonal β -phase. Formation of a tetragonal phase with distinct a and c lattice parameters occurs below 290 K in agreement with DSC data, which shows a phase transition centered at 290 K (see supplementary information S6, Figure S4). The width of the DSC peak centered at 290 K indicates a very slow transition occurring between 310 K and 273K. This slow transition reflects the glassy nature of hybrid halide perovskites, with the central organic cation known to exhibit slow, glass-like reorientational dynamics leading to disordered phases³³⁻³⁶. The width of this phase transition could be a source of the confusion as to the room temperature structure of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ ¹⁷⁻²⁰.

Below 180 K in the NPD data, the intensity of some of the emergent peaks decreases (see the (211) hkl values reflection near 3.35 Å in Figure 2a) corresponding to the transformation to an orthorhombic γ -phase and ongoing cooling of this phase. The origin of the loss in intensity in reflections such as the (211) is likely to be associated with the convergence of the reduced a and c lattice parameters (see Figure 1) in this temperature regime; the intensity of such reflections will be dependent on differences in the degree of tilting of the PbI_6 octahedra along the a and c lattice directions and as these two converge the reflection intensity is reduced. However, full analysis would require a detailed modeling of the iodide positions over this temperature range which is beyond the modeling than can be justified with the data resolution and quality available.

Trends in the shift and intensity of peaks were investigated using sequential refinement in GSAS II²⁶. A pseudo-cubic model was first used from the refinement of NPD data at 300 K; however, it became apparent that a tetragonal model would better describe the structural behavior over the vast majority of the temperature range investigated. The β -phase tetragonal model obtained from a long collection at 200 K and based on that developed by Weber *et al.* for FAPbI_3 and was used²¹. The tetragonal space group $P4/mbm$ was used, and the part deuterated FA cation was modelled as a rigid CH-NHD molecule. In this model the carbon atom of the formamidinium cation is assigned to a site with coordinates (0.5, y ,0.5) with $y \sim 0.5$ and refinement showed that $y=0.5$ within the extracted error. The Cs^+ cation will also occupy a site very close to (0.5, 0.5, 0.5) and Cs and C have similar neutron scattering lengths (5.42 fm and 6.64 fm). This means that, with the low level of Cs, developing a structural model which had a distinct Cs site with a site occupancy of 0.1 was not justified – indeed attempts to do this and refine a model with both Cs and FA cations result in an unstable, non-converging refinement. Therefore, the model used in the analysis used a central carbon site at (0.5, y ,0.5) with $y \sim 0.5$ to represent both the 90% formamidinium carbon and 10% Cs; note that this modeled the profile peak intensities well and did not, of course, affect the extracted information such as crystal system or lattice parameters.

This model was refined against shorter NPD collections at higher temperatures but failed to provide a suitable fit above 280 K, corresponding with the slow second order transition to the cubic α -phase. The model was subsequently refined again against the 280 K NPD pattern, which was used as a starting point to the sequential refinement covering all data sets collected below this temperature. Lattice parameters extracted as a function of temperature from the sequential refinement are shown in Figure 1b.

The evolution (positions and halfwidth) of the dominant peak centered at 3.15 Å (Figure 2a) was also analyzed using sequential peak fitting in GSAS II. Changes in the position of this peak position and its FWHM correspond to the phase transition points suggested by the earlier sequential refinement of a pseudo-tetragonal structure. These changes in gradient of the peak shift (Figure 2b) are observed at 290 K, 180 K and 125 K corresponding with the cubic, tetragonal, orthorhombic and disordered low temperature phases respectively. Peak broadening can be used as an indicator for peak splitting corresponding to changing symmetry. Extracted values of the dominant peak full width at half maximum (FWHM) as a function of temperature (Figure 2c) indicate clear broadening below 290 K which can be assigned to the formation of distinct peaks indicative to the tetragonal structure. An abrupt change in FWHM shift is observed at the orthorhombic transition by 180 K. This is an artifact of modeling the true orthorhombic structure with a tetragonal unit cell in which the a and c lattice parameters (see Figure 1) are rapidly converging. The reflection at 3.15 Å is the (200) reflection and equivalents in the room temperature cubic phase. This splits into the (200) and (002) reflections for the tetragonal phase and further for the orthorhombic description. The convergence in the positions of the (200), (020) and (002) reflections and equivalents as the c lattice parameter decreases rapidly on cooling from

180 K. Example profile fits obtained during the SEQGSAS refinements, at 112 K, 145 K, 225 K and 255 K are included in the supplementary information, S9.

3.3 Cubic α -Cs_{0.1}FA_{0.9}PbI₃, > 290 K: The structure of Cs_{0.1}FA_{0.9}PbI₃ above 290 K was investigated via NPD, PXRD and SXRD.

Fully hydrogenated, phase pure Cs_{0.1}FA_{0.9}PbI₃ samples synthesized by the inverse solubility method, and ground using a pestle and mortar, were investigated using PXRD at RT. PXRD patterns indexed best to the cubic $Pm\bar{3}m$ space group and revealed a shift in the (100) peak in comparison to α -FAPbI₃ due to an expected contraction of the lattice on Cs incorporation¹⁸. Figure 3b shows the indexed PXRD pattern obtained at 298 K from a STOE STADI P diffractometer. PXRD was also used to check the quality of part deuterated samples synthesized by the drop casting method for NPD measurements. Impurity peaks were identified and indexed to small quantities (< 2%) of δ -CsPbI₃ and δ -FAPbI₃ (see supplementary information, S4).

NPD data obtained at 300 K from a 2-hour collection on POLARIS at the ISIS neutron and muon source was fully analyzed using the GSAS II software. Lattice parameters from the indexed PXRD data were used as a starting point for further refinement.

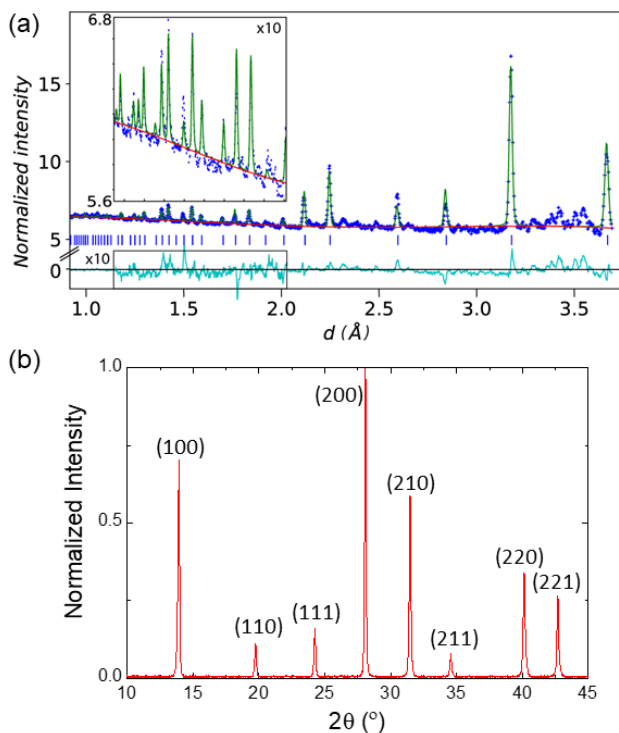


Figure 3. (a) Rietveld fit (red) on NPD data (blue) collected on POLARIS at 300 K and (insets, boxed) enlarged areas, x10, of fit between d -spacing 1.2 – 2 Å. Data were refined to space group $Pm\bar{3}m$ with lattice parameter $a = 6.34562(24)$ Å, $wR = 1.69\%$. The difference between the observed and calculated values is shown in light blue. Regions between 2.32 Å – 2.44 Å and 3.44 Å – 3.56 Å could be assigned to δ -phase impurities. (b) PXRD data indexed to a cubic cell in $Pm\bar{3}m$.

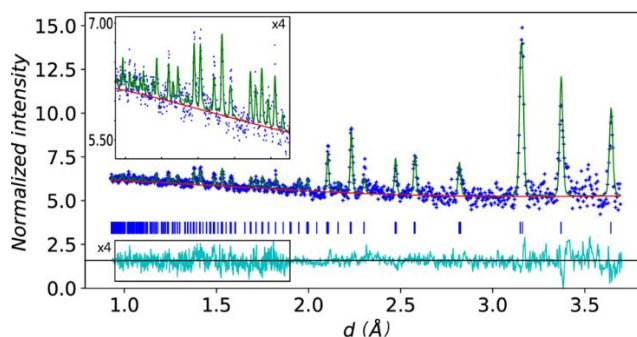


Figure 4. Rietveld fit on NPD data collected on POLARIS at 200 K and (insets - boxed) enlarged areas, x4, of fit between d -spacing 0.9 – 1.9 Å. Data were refined to space group $P4/mbm$, $a = 8.9084(8)$ Å $c = 6.3224(8)$ Å, $wR = 2.90\%$. Regions between 2.32 Å – 2.44 Å and 3.44 Å – 3.56 Å could be assigned to δ -phase impurities.

Initially the structural description of the FA cation in FAPbI₃ at 298 K was used as a model⁷, atomic positions were used as published and only lattice and instrumental parameters were varied at first. The planar part-deuterated FA cation was modelled to a rigid H-C-N-HD molecule, with initial isotropic atomic displacement parameters (ADPs) of 0.5 Å² set. As performed by Weller *et al.*⁷ for FAPbI₃, the C-H atoms were assigned a site occupancy of 0.16, while the single N-HD group was modelled with an occupancy of 0.0833, together describing the 12 orientations of the planar FA cation within the cuboctahedral void. As described for the tetragonal phase analysis the Cs⁺ cation was not modeled independently but represented by the carbon atom of a fully occupied FA site. This initial refinement produced a good fit of the data, with a wR of 1.92%. Subsequent refinement of the Pb and I ADPs produced a slightly improved fit, with wR of 1.89%. The ADPs of the C, N, H and D making up the rigid FA cation were constrained to be equal, and when refined, the wR improved to 1.72% leading to a value of 0.244(6) Å². The high thermal parameter values indicate significant rotational motion of the FA cation at 300 K. The position of the whole cation was then refined, producing the cubic structural model detailed in the supplementary information, in space group $Pm\bar{3}m$ with lattice parameter $a = 6.34562(24)$ Å, wR 1.69%. Further crystallographic information is given in the supplementary information S5 and associated CIF. Despite some earlier studies suggesting Cs_{0.1}FA_{0.9}PbI₃ adopts a tetragonal structure in ambient conditions¹⁹, we do not observe peak splitting in this high-resolution data that would indicate tetragonal symmetry.

Single crystals of α -Cs_{0.1}FA_{0.9}PbI₃ grown via inverse solubility were selected to obtain a structural model at 300 K using SXRD data. Two methods were used. Firstly, the established structure for α -FAPbI₃ was used as a model, accounting for the low scattering and tumbling of the FA cation by modelling the A-site as a single atom with a large ADP. Secondly, the structure was solved in the low symmetry space group $P\bar{1}$ before the validation software PLATON was used to determine a more suitable space group. In both cases the best solution fit to $Pm\bar{3}m$ with lattice parameter $a = 6.2780(3)$ Å. Generated (pseudo-) precession figures, supplementary information S10, also confirmed the cubic symmetry at 300 K.

Large anisotropic ADPs associated with on axis iodine atom in the SXRD refinement suggest significant oscillation of the PbI_6 octahedra. An attempt was made to model the observed spread of electron density to locked octahedral tilts as predicted from *ab initio* methods by Gosh *et al.*¹⁸; however, any ordered tilting of the PbI_6 octahedra could not be modeled. We therefore resolved that the time averaged structure of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ is cubic at 300 K, although the local structure may contain pseudo-tetragonal domains due to tilted octahedra switching rapidly between preferred directions. Pair distribution function analysis has shown the Pb^{2+} cation to be displaced at ambient temperatures in FAPbI_3 resulting in concerted displacement of the iodide anions³⁷ and these displacements potentially contribute to the extracted large ADPs modeled in our SXRD measurements on $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$. However we do not have the resolution in our NPD data to model such local order. Further studies probing the local structure of these complex materials would be valuable including high-resolution XRD measurements investigating displacements of the B and X-site anions and cations would be useful.

3.4 Tetragonal Phase, β - $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$, 290 K – 180 K: Variable temperature NPD was used to investigate the tetragonal β -phase that was found to exist between 290 K and 180 K; the transition to this phase is characterized by the appearance of the tetragonal unit cell (211) reflection as seen centered at $d = 3.37$ Å in Figure 4. Rietveld fits were performed on NPD data collected at 200 K and based on the model developed by Weber *et al.* for pure FAPbI_3 ²¹. The part-deuterated FA cation was modeled as a rigid H-C-N-HD molecule with an occupancy of 0.5 for the C atom and 0.25 for the N, H and D, representing the restricted motion of the cation in the tetragonal phase²¹. ADPs for the Pb and I were then refined, producing lower values than those obtained in the cubic phase, suggesting reduced motion of the PbI_6 octahedra. The thermal parameters for C, N, H and D of the FA cation were constrained to be equal, refining to give $0.190(9)$ Å². The position of the rigid cation was then refined to give the tetragonal structural model described in the supplementary information and associated CIF, S5. The refinement converged to a cell in the space group $P4/mbm$, lattice parameters $a = 8.9084(8)$ Å and $c = 6.3224(8)$ Å, $wR = 2.90\%$. The tetragonal model fits the data well from 180 K to 280 K, above this temperature refinements failed as the material gradually transitioned to the cubic α -phase. Additional example profile fits obtained during these SEQGSAS refinements, at 225 K and 255 K are included in the supplementary information, S9.

3.5 Y- $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ phase 180 K – 125 K: The structure of the parent phase FAPbI_3 can be modelled using a tetragonal unit cell for all temperatures below 180 K^{21, 38, 39}. Analysis of the SXD data obtained from $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ at 175 K and 150 K showed the issues normally found for perovskitic phases of this type which undergo a phase transition to a lower cell symmetry on cooling. As has been observed for FAPbI_3 , it seems that $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ forms crystallographic twins when cooled through phase transitions, leading to large residuals and challenges identifying the absolute structure²¹. Thus SXRD data obtained at 175 K could be indexed to either crystallographic twins in the tetragonal

space group $P4/mbm$, or orthorhombic $Pnma$. Refined lattice parameters for the orthorhombic description were $a = 8.8217(16)$ Å, $b = 12.5912(17)$ Å and $c = 8.7242(16)$ Å. Example profile fits obtained during the SEQGSAS refinements, at 112 K and 145 K, are included in the supplementary information, S9.

For SXD data collected at 150 K the best fits using an orthorhombic space group; $Pnma$ at 150 K where lattice parameters extracted were $a = 8.8192(12)$ Å, $b = 12.5777(13)$ Å and $c = 8.6274(13)$ Å; however a crystallographically twinned tetragonal model in $P4/mbm$ could not be fully discounted. Note that in both these structural models that $c/\sqrt{2} \times a$ is less than 1.01 supporting the observation that these models could not be distinguished from tetragonal in the neutron powder diffraction study. In addition, these data support the observation of a rapid decrease in the c lattice parameter in this temperature range – as seen in the NPD data, Figure 1b.

3.6 Low Temperature Phase, < 125 K: SXRD data collected at 120 K converged to the space group $Pnma$ with lattice parameters $a = 8.8215(11)$ Å, $b = 12.5815(13)$ Å, $c = 8.6091(13)$ Å. However, unlike the higher temperature data, additional weak reflections were observed at 120 K which could be attributed to the formation of a disordered state. The emergence of disorder at low temperature agrees with previous findings for FAPbI_3 in which residual entropy causes the freezing of FA cation rotation and locking of the PbI_6 octahedra in a glass-like state^{21, 33-37, 39}. As with the parent phase FAPbI_3 some elements of long range ordering associated with the cations or, more likely, the tilting of the PbI_6 octahedra persist below 120 K - this generates the observed additional diffraction intensity seen for $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$.

3.7 Variable Temperature PL: A single crystal of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ synthesized via the inverse solubility method was mounted in a cryostat and illuminated with an excitation wavelength of 630 nm while the temperature was varied from 290 K to 25 K. Each PL spectrum was fitted with a single Gaussian function subsequently used to analyze the peak PL positions and FWHM (Figure 5a, b, c). It should be noted that spectra taken at 290 K and 275 K were fitted using a second Gaussian term to account for photon reabsorption effects in the 1 mm thick crystal⁴⁰. These reabsorption peaks were not included in the peak PL position and FWHM analysis.

Peak positions extracted from Gaussian fits of the PL were plotted as a function of temperature (Figure 5b) revealing a red shift with decreasing temperature familiar to these family of hybrid halide perovskites^{41, 42}. This shift has been attributed to stabilization of the valence band maximum due to a combination of thermal expansion effects and electron-phonon interactions⁴³. Below 125 K a blue shift in peak position is observed. Interestingly the blue shift at low temperatures correlates with the transition to the disordered state as revealed through XRD and NPD measurements presented in this work. A change in PL shift at low temperature has been previously linked to disorder in MAPbX_3 hybrid halide perovskites, attributed to band filling effects induced

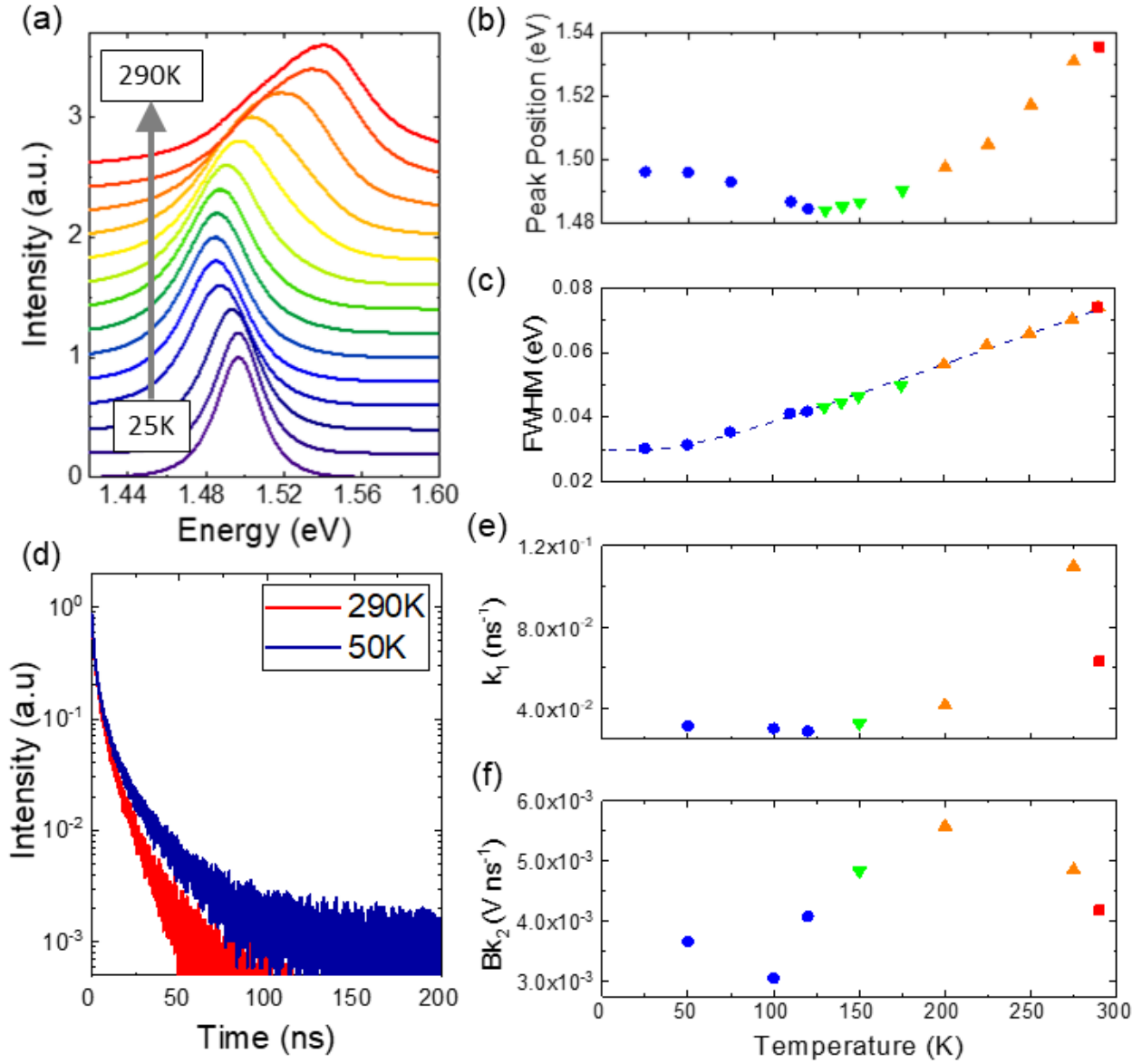


Figure 5. (a) Variable temperature steady state PL on a single crystal of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$. (b) Peak positions and (c) FWHM of the Gaussian fits to PL as a function of temperature. (d) PL decay measured at 290 K and 50 K. (e) Extracted monomolecular recombination rate constants (k_1) and (f) effective bimolecular rate constant (Bk_2) from fits to variable temperature PL decay. Points are colored according to the cubic α -phase (red square), tetragonal β -phase (orange triangles), orthorhombic γ -phase (green inverted triangles) and disordered low temperature phase (blue circles).

by a difference in band gap between domains of ordered and disordered cation orientations⁴¹.

The temperature dependence of the PL FWHM ($\Gamma(T)$) can be expressed in terms of the below^{42,43}:

$$\Gamma(T) = \Gamma_0 + \frac{\gamma_0}{\exp\left(\frac{E_{LO}}{K_B T}\right) - 1} \quad (1)$$

where T is temperature, K_B is the Boltzmann constant, Γ_0 is the temperature independent homogeneous broadening term γ_0 is the charge carrier longitudinal-optical (LO) phonon coupling strength and E_{LO} is the energy for the LO phonon. The resulting FWHM of the Gaussian fits to the steady state PL could be modelled to Equation 1 (blue dashed line in Figure 5c), from which the extracted values for Γ_0 , γ_0 and

E_{LO} were 29 ± 1 meV, 30 ± 4 meV and 13 ± 1 meV respectively. There is possible grouping of the FWHM data according to phase in Figure 5c; however, the discontinuities are small and proved difficult to model separately. Transient luminescence spectra for $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ were measured at seven distinct temperatures between 290 K and 50 K inclusive (Figure 5d). The resulting spectra were modelled according to the charge-carrier recombination rate equation⁴⁴:

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_3 n^3 \quad (2)$$

where n is the photogenerated carrier density and k_i is the recombination rate. Each term represents a charge carrier annihilation process following excitation, (1) being

monomolecular recombination, (2) bimolecular recombination and (3) three body Auger recombination. Previous studies have shown first and second order recombination mechanisms to dominate in hybrid perovskites at moderate intensities, therefore Auger recombination was neglected⁴⁵.

Values of k_1 , determined from fitting PL decay with equation 2, are shown in Figure 5e. The monomolecular term is predominately determined by first order Shockley-Reed recombination in hybrid halide perovskites, therefore the value of k_1 is dictated by trap-assisted recombination⁴⁴. In general, the k_1 decreases with decreasing temperature; however, a significant increase is seen between 290 – 275 K. This was potentially due to domains of cubic and tetragonal phases appearing over the phase transition and acting as recombination centers. Below the 125 K transition into the disordered structure the monomolecular recombination rate increases, possibly due to disordered domains acting as recombination centers^{41,44}.

Effective values of the bimolecular rate constant were measured as Bk_2 ⁴⁶, where B is a proportionality constant as described in the supplementary information, S7. The values of Bk_2 (Figure 5f) generally increase with decreasing temperature, until the transition to the low temperature disordered phase around 125 K. The reversal in trends observed for PL peak position, k_1 and Bk_2 below the 125 K transition clearly indicate the disordered nature of the FA cations and PbI_6 orientations at low temperature affect the optoelectronic properties of the material. It is speculated that the presence of disordered domains act as recombination centers, so increasing the monomolecular and bimolecular recombination rates⁴⁴.

4. DISCUSSION:

The results of the investigation into the phase behavior of bulk $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ are combined with those found for phase pure α -FAPbI₃ and α -CsPbI₃ to produce the phase diagram in Figure 6^{10,21}. Cs and FA cation mixing is more energetically favorable in the α -phase than δ -phase¹⁶, leading to the preferred formation of cubic α - $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ through synthesis by inverse solubility and precipitation from acid. Mixed Cs-FA crystals and powders remained stable in the black α -phase in air at 20% humidity over one month. PXRD measurements on $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ powders used in powder diffraction experiments showed negligible degradation or phase separation to δ -FAPbI₃ and δ -FAPbI₃ over 28 days (see supplementary information for PXRD measurements, S8). It was observed that after six months that partial phase separation had occurred in the mixed Cs-FA samples forming small regions of yellow δ and black α -phase. This stability is much improved on that of α -FAPbI₃, which quickly transforms to δ -FAPbI₃ on exposure to the atmosphere⁷. Lee *et al.* attributed the improved stability of $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ to stronger interactions between the FA cations and I anions due to a contraction of the unit cell⁴⁷.

A consequence of the improved stability of the mixed Cs-FA lead iodide perovskite is that the desirable black α -phase

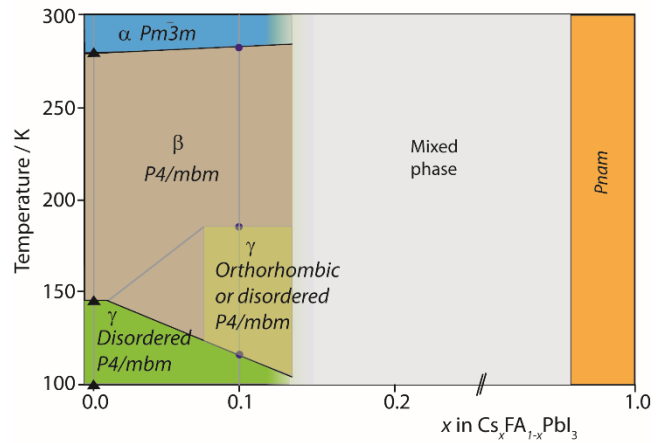


Figure 6. Schematic phase diagram for $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ solid samples with estimated phase transition positions. Space groups and transition temperatures as found in this work (blue circles) from variable temperature NPD data on $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ are compared with that found by Weber *et al.*²¹ for FAPbI₃ (black triangles) and Sutton *et al.*¹⁰ for CsPbI₃.

becomes more accessible under ambient conditions. Numerous studies have shown the tetragonal (β) to cubic (α) transition in quench cooled samples of α -FAPbI₃ to occur at 285 K^{21,38,39}. However, this transition is rarely observed as formation of the hexagonal δ -FAPbI₃ phase is energetically favored at room temperature⁷. The variable temperature NPD data presented in this paper shows the tetragonal (β) to cubic (α) transition temperature only slightly affected by the addition of 10% Cs into the FAPbI₃ structure, determined as 290 K for $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ in this work.

There has been confusion whether $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ adopts a cubic or tetragonal structure at room temperature¹⁸⁻²⁰. Variable NPD data of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ suggested a slow, second-order transformation from the cubic α -phase to a tetragonal phase centered close to 290 K. The proximity of the cubic-tetragonal transition to room temperature, in combination to the dynamic nature of the PbI_6 octahedra, is likely to be a key factor as to why these differences in the reported room temperature structure of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ occur in the literature.

Ab initio studies have shown that addition of the smaller Cs cation into the FAPbI₃ structure results in a contraction of the cuboctahedral voids formed by the corner sharing PbI_6 octahedra, resulting in geometric strain of the lead iodide framework, and leading to stronger hydrogen bonding between the amine groups of the FA cation and iodide¹⁸. These effects lead to the suppressed motion of the FA cation, and locked tilting of the PbI_6 octahedra at lower temperatures^{17,18}, inducing the possible formation of an additional orthorhombic γ -phase as seen in the variable temperature SXRD; the formation of an orthorhombic phase would also be consistent with the changes observed in the NPD data between 170 and ~125 K. As well as the appearance of this extra orthorhombic phase, the addition of Cs lowers the transition to a low temperature disordered state from 140 K observed in pure FAPbI₃, to 125 K as suggested by NPD, SXRD and PL for $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ in this work. Therefore, in addition to increasing resistance to δ -phase formation, incorporating Cs into the FAPbI₃ structure has important effects

resulting in the desirable cubic α -phase being accessible at room temperature, the stabilization of an orthorhombic phase below ~ 180 K and lowering of the transition temperature to the disordered state below 125 K.

5. CONCLUSIONS:

The phase behavior of formamidinium lead iodide partially substituted with cesium ($\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$, $0 \leq x \leq 0.2$) has been investigated. PXRD data showed contraction in the lattice parameter when compared to pure FAPbI_3 indicating successful Cs incorporation for $x < 0.15$, and EDX measurements suggested the preferential formation of the composition $\text{Cs}_{0.12}\text{FA}_{0.88}\text{PbI}_3$ in high quality crystals synthesized by inverse solubility methods. From variable temperature NPD it was determined that inclusion of Cs results in formation of the desirable cubic α -phase of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ that exists at room temperature. Moreover, the formation of an orthorhombic phase is inferred on cooling below 180 K, and disorder attributed to residual entropy of FA cation orientation appeared only on cooling below 125 K. Our extensive study provides important insights into the intrinsic behavior of mixed cation perovskites commonly used in photovoltaics.

ASSOCIATED CONTENT

Supporting Information. Additional synthetic details, Energy dispersive X-ray spectroscopy, differential scanning calorimetry, additional structural models and photoluminescence modelling. Data created during this research are freely available from the University of Bath data archive at <https://doi.org/10.15125/BATH-00715>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. B.C. undertook sample synthesis. L.E.H., B.C. and C.C.W. the X-ray diffraction experiments and analysis. B.C., M.T.W. and P.F.H. the neutron diffraction experiments and analysis. B.C., S.R., J.F. and D.W. performed the photoluminescence experiments and analysis.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MA, methylammonium; FA, formamidinium; PXRD, powder X-ray diffraction; SXR, single crystal X-ray diffraction; NPD, neutron powder diffraction; PL, photoluminescence

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